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OPTIMAL STRATEGY SEARCHING FOR A COMPONENT COMPOSITION OF SYNTHETIC SODIUM SILICATES USED IN THE PRODUCTION OF MICROSPHERES

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The results of synthesis of a sodium silicate batch for microspheres in an aqueous medium using sol-gel technology are described. It is demonstrated that crystalline phases marked on the Krachek diagram have been formed without high-temperature treatment. A nomogram has been developed, which is recommended for designing glasses to model a phase composition based on a preset silica modulus and a structure cohesion factor taking into account the effect of Na_2O and SiO_2 on glass properties, to determine the range of probable glass formation, and to optimize the technological process.

The Na_2O – SiO_2 system is a basis for the majority of industrially produced glasses and microspheres used in laser physics experiments. Researchers at the Russian Federal Nuclear Center in producing microspheres use the liquid drop and the frit methods, in which drops of a solution containing glass-forming components or particles of milled xerogel are heat-treated in the channel of a vertical tube furnace about 5 m high at a temperature from 150 – 250 to 1100 – 1300°C (RF patent No. 2036171); next, finished glass microspheres are collected at the exit from the furnace into a special checker and later filled with gaseous hydrogen isotopes [1]. At the beginning of the technological process a solution of glass-forming components is prepared according to the method described in [2, 3]. The phase composition and structure of material and, finally, the properties of the products (gas permeability atmosphere resistance, etc.) depend on the thoroughness of synthesis performed.

Depending on the ratio between the main components, i.e., SiO_2 (glass-forming agent) and Na_2O (modifier), as well as temperature conditions, the phase composition of sodium silicate is set based on the Krachek diagram [4]. However, this diagram in itself is insufficient for determining the probability of glass formation and, furthermore, synthesis of material using the sol-gel method does not include high-temperature treatment.

The present study attempts to complement the Krachek diagram with data on calculating silica modulus n_{Si} and Ermolenko structure cohesion factor Y to study the phase composition of sodium silicates obtained in an aqueous medium using sol-gel technology, to determine the possibility of glass formation, and to predict some properties.

The following formulas were used in calculations [5, 6]:

$$n_{Si} = \frac{x_{SiO_2}}{x_{Na_2O}}; \quad (1)$$

$$Y = \frac{\sum_j m_j x_j z - \sum_k m_k x_k}{\sum_j m_j x_j}, \quad (2)$$

where x is the molar content of an oxide, %; m is the number of cations in the oxide; j and k are oxides containing cations with a quantity of bonds more than 1 and equal to 1, respectively; z is the valence (coordination number).

Selecting a silica modulus, the engineer sets the ratio of SiO_2 to Na_2O forming the crystalline phase of the main structural pattern of the sodium-silicate glass designed, whereas the values of the Y factor determines the average number of bridge oxygen ions in structural polyhedrons and predicts the dimensionality of the lattice and the possibility of glass formation: with $Y = 4$ the lattice is three-dimensional; with $Y = 3$ it is a two-dimensional laminar lattice, and with $Y = 2$, a one-dimensional chain lattice. With $Y < 2$ glass formation is impossible due to formation of short (for instance, binary) chains or isolated "insular" fragments [6]. Note that the term "two-dimensional structure" is conventional enough, since silicates are based on the silicon-oxygen tetrahedron, which is a three-dimensional polyhedron; therefore, it is more accurate to speak of the formation of a three-dimensional layer of a significant extent, whose surface area significantly exceeds its thickness. Thus, both criteria logically complement each

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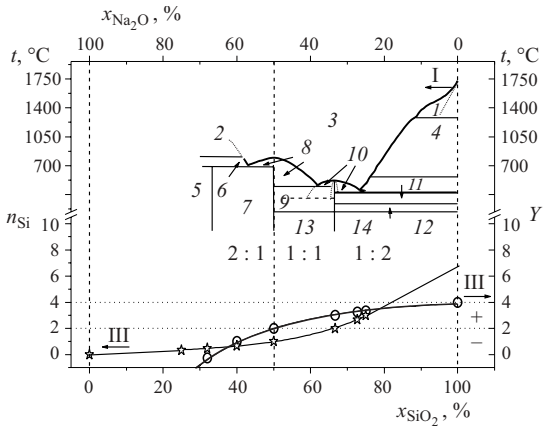

Fig. 1. Nomogram for determining silica modulus n_{Si} (II), Ermolenko structure cohesion factor Y (III), and phase composition of synthesized batch according to Krachek diagram (I). Phase and its area: *1*) α-cristobalite + liquid phase; *2*) Na_2O + liquid phase; *3*) liquid phase; *4*) α-tridimite; *5*) $Na_2O + 2Na_2O \cdot SiO_2$; *6*) $2Na_2O \cdot SiO_2$ + liquid phase; *7*) $2Na_2O \cdot SiO_2 + Na_2O \cdot SiO_2$; *8*) $Na_2O \cdot SiO_2$ + liquid phase; *9*) $Na_2O \cdot SiO_2 + \alpha\text{-}Na_2O \cdot 2SiO_2$; *10*) $Na_2O \cdot 2SiO_2$ + liquid phase; *11*) α-quartz + liquid phase; *12*) $\alpha\text{-}Na_2O \cdot 2SiO_2$ + α-quartz; *13*) $\beta\text{-}Na_2O \cdot 2SiO_2$; *14*) $\beta\text{-}Na_2O \cdot 2SiO_2$ + α-quartz; possible "+" and impossible "–" glass formation areas according to Y factor.

other and determine the type of a structure, its cohesion or looseness. This is responsible for glass properties and application areas of glass products. Modeling structure makes it possible to optimize the ratio of the main components, increase the accuracy of the calculation of glass compositions, and minimize the number of verification experiments.

According to the Krachek diagram, there are 10 main phases in the $Na_2O - SiO_2$ system. The silica modulus and the structure cohesion factor were calculated for each of them, including pure sodium and silicon oxides, based on formulas (1) and (2) (Table 1). Figure 1 shows the phase diagram and curves of silica modulus and cohesion factor variations.

Analysis of experimental data and calculations performed revealed the following. If the main phases of a projected composition belong to the phase diagram area on the left of the vertical 1 : 1 ($x_{Na_2O} : x_{SiO_2} = 50 : 50$), the probability of glass formation is negligible, since in this case $n_{Si} < 1$ and $Y < 2$, and accordingly single fragments $[(SiO_4)Na_4]$ and/or two-term chains $[(Si_2O_7)Na_4]$ are formed, which do not have bridge oxygen ions:

$$2Na_2O + SiO_2 \rightarrow [(SiO_4)Na_4];$$

$$2[(SiO_4)Na_2]^{2-} + 2[(SiO_4)Na_2]^{2-} + SiO_2 \rightarrow 2[Na_2(O_3SiOSiO_3)Na_2] + [SiO_4].$$

Evidently, one should select the phase diagram area that is to the right of boundary 1 : 1 when designing compositions for vitrification.

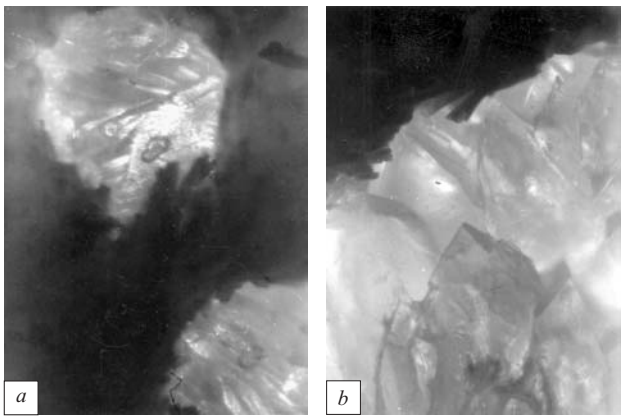

Fig. 2. Crystal sodium silicate phases in dry material (× 54): *a*) traces of drop liquation; *b*) crystals of different habitus.

Batch components for microsphere production were obtained using sol-gel technology in an aqueous medium. First, the silica modulus ($2 < n_{Si} \le 3$) and the weight of the batch were specified. Based on these values, the weight of silicon acid and sodium hydroxides samples for synthesis were calculated. We were not able to obtain compositions with $n_{Si} > 3.4$ (the upper bound of synthesis), i.e., the formation of high-silica silicates ($x_{SiO_2} \ge 75$ %) is highly improbable. The final solution was dried in air at ambient temperature. As the solvent was removed and the material became concentrated, its separation occurred in the form of drops and ended in crystallization.

It can be clearly seen in the photos of dry residual (Fig. 2, photos taken using a MIK-4 microscope and a Zenit camera) that crystals in the matrix and in drops have perceptibly different habitus. After storage in air for 5 years (the materials was obtained in 1998) no carbonate corrosion of crystals inside the drops was registered, which is evidence of synthesis of sodium silicate rich in silica. According to x-ray phase analysis data using a RIGAKU Dmax/RC diffractometer (Japan),[2] the main phases of the binary sodium-sili-

[2] Results of analysis have been supplied by N. D. Sevryugina and M. Yu. Sidorkin, researchers at the Russian Federal Nuclear Center.

TABLE 1

Crystal phase	Phase diagram area	x, %		n_{Si}	Y
		SiO_2	Na_2O		
Na_2O	2, 5	0	100.00	0	$-\infty$
$3Na_2O \cdot SiO_2$	2, 5, 6	25.00	75.00	0.33	– 2.00
$2Na_2O \cdot SiO_2$	5, 6, 7	31.96	68.04	0.47	– 0.26
$3Na_2O \cdot 2SiO_2$	6, 7	40.01	59.99	0.67	1.00
$Na_2O \cdot SiO_2$	7, 8, 9	50.00	50.00	1.00	2.00
$\alpha\text{-}Na_2O \cdot 2SiO_2$	9, 12	66.67	33.33	2.00	3.00
$3Na_2O \cdot 8SiO_2$	11, 12, 13, 14	72.70	27.30	2.66	3.25
$Na_2O \cdot 3SiO_2$		75.00	25.00	3.00	3.33
α-quartz	1, 11, 12, 14	100.00	0	$+\infty$	4.00
α-tridimite	4				

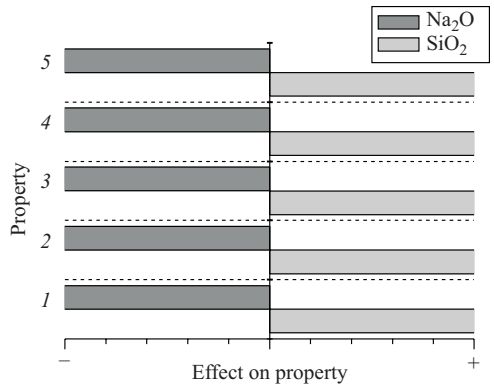

Fig. 3. Histogram of the effect of Na_2O and SiO_2 on glass properties: *1*) melting temperature; *2*) viscosity; *3*) propensity for crystallization; *4*) mechanical properties; *5*) chemical resistance; positive "+" and negative "–" effect.

cate composition with $n_{Si} = 3$ are $Na_2O \cdot SiO_2$ (α and β forms), $Na_2O \cdot 2SiO_2$, and Na_2CO_3; besides, $2Na_2O \cdot SiO_2$ and SiO_2 are identified as impurities. As a consequence of synthesis of multicomponent batches containing silicon, sodium, lithium, potassium, and lead oxides and citric acid, as well as batches without PbO and citric acid, the above listed main phases and $Na_2O \cdot SiO_2 \cdot 5H_2O$ were formed; the composition of the impurities did not change (the present study considers only sodium silicates). With $n_{Si} < 3$ the ratio between the mono- and disilicate shifted toward the former phase.

Thus, synthesis by the sol-gel method with a preset silica modulus ($n_{Si} = 3$) produced the same crystal phases as those formed according to high-temperature technology (Fig. 1, the Krachek diagram). In the course of the experiments a process similar to liquation took place, whose probability was noted in [4]. The presence of carbonate and orthosilicate related to the phase diagram area on the left of the vertical line 1 : 1 suggests that a phase rich in the alkaline component was formed, as well as sodium oxide as an independent phase reacting with carbon dioxide from ambient air. Furthermore, its is highly probable that part of NaOH did not react with silicic acid and created an alkaline medium (conditions) for base reactions [2, 3].

The structure cohesion factor of the mono- and disilicate, whose formation was analytically confirmed, was equal to 2 – 3. This satisfies the condition of glass formation [6] and points to the probability of formation of a laminar two-dimensional structure with fragments of a three-dimensional skeleton. The glasses developed do not belong to the group of high-silica glasses, they have satisfactory gas permeability, and they are used in laser physics studies. After protracted storage in air, traces of carbonate corrosion are registered on the surface of microspheres, i.e., their atmospheric resistance is insufficiently high. However, it should be noted that chemically resistant quartz glass and glasses rich in silica are the most gas-permeable [7]. They typically have the following parameters: $n_{Si} \to +\infty$, $Y \to 4$, the phase composition belonging to the Krachek phase diagram area to the left of boundary 1 : 3, i.e., $x_{Na_2O} : x_{SiO_2} = 25 : 75$ (Fig. 1 and Table 1). Figure 3 shows a histogram illustrating the opposite effects of Na_2O and SiO_2 on some properties of glass (based on data in [8]). This histogram was used as an additional information source in designing chemical compositions for microspheres.

Thus, liquid-phase synthesis of glass batch for microspheres is possible at $n_{Si} = 1.0 – 3.4$; when $n_{Si} < 1$ and the cohesion factor $Y < 2$, glass formation is impossible; at $n_{Si} > 3.4$ and $Y < 3$ glass formation is probable, but such solutions have not been obtained. Modeling and analysis of the phase composition of glasses in the $Na_2O – SiO_2$ system calculated based on a preset silica modulus and a respective structure cohesion factor, taking into account data on the effect of Na_2O and SiO_2 on glass properties, made it possible to identify an optimum strategy for searching for the main components of glass compositions, justify a need for compromise solutions, minimize the number of verification experiments, and eliminate unjustifiable consumption of reactants. The nomogram that has been developed is recommended for designing glasses.

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